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Iowa State University

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Progress:

During this period, we concentrated on improving the stability of a-Si devices by using chemical annealing techniques. Chemical annealing technique was claimed by the Shimizu group to produce materials with significantly improved stability. We decided to try to replicate these results by using chemical annealing with He.

The films and i layers in devices were deposited using a layer-by-layer deposition method, using the low pressure ECR reactor described earlier. The growth cycle was generally 8 or 10 seconds, during which the flow of silane was set to ON. During the growth cycle, the gases used were silane, hydrogen and helium. Then, for different anneal periods, only helium was present in the reactor. The plasma was continuously on during the growth and anneal cycles. The growth cycle was such as to grow about 2-3 nm thick films. The anneal cycle times were systematically varied between 10 and 60 seconds.

There were no significant changes to either device or film properties when the anneal cycle time was 10 seconds. However, when the anneal cycle time was increased to 20 seconds and beyond, the films became nanocrystalline. This was a surprising result, since during annealing, only helium was flowing. The crystalline signature of both films and devices was verified using both Raman spectroscopy and x-ray diffraction. The devices showed all the characteristics of nanocrystalline base layers, including QE extending out towards the infrared region, and the voltage in the device reducing to the 0.5 V range from the typical 0.8+ V for a-Si:H.

In contrast to He, when hydrogen was used during both the growth and annealing cycles, no crystallization resulted. We are still investigating whether the bandgap etc. changed during the hydrogen anneal.

These are very remarkable results, since we have shown that one can grow nanocrystalline materials *without* significant hydrogen dilution. We have therefore disproved the standard model for growth of nanocrystalline Si. The hydrogen in the film during deposition (~10%) is enough to cause crystallization when enough ion bombardment is provided. From Langmuir probe measurements, we know that the He ion is more energetic than the hydrogen ion, plus it has a higher mass. This combination of higher energy and higher mass seems to be enough to crystallize thin films of a-Si:H.

We will be exploring these results in further detail during the upcoming quarter, including the search for greater stability in a-(Si,Ge):H alloys.

The results are described in more detail in the appendix.

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Nanocrystalline Si Films and Devices Produced Using Chemical Annealing with Helium

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ABSTRACT

We report on growth of nanocrystalline Si:H films and devices using a layer-by-layer growth technique, where the growth of a thin amorphous layer by PECVD is followed by chemical annealing in a Helium plasma. The films and devices were grown using a remote, low pressure ECR plasma process. It was found that the structure of the films grown using the layer-by-layer technique depended critically upon whether the annealing was done with hydrogen or helium, and the time taken to do the annealing. When the annealing was done in a hydrogen plasma, the films remained amorphous; in contrast, when the annealing was done in helium, and the annealing time was increased to 20 seconds from 10 seconds, the films became crystalline. The crystallinity of the films was confirmed using Raman spectroscopy and x-ray diffraction. The result obtained here shows that it is not necessary to have a high hydrogen dilution to obtain nanocrystalline films. Rather, the amount of hydrogen already present in an amorphous film is enough to cause crystallization, provided that enough ion flux and perhaps energy are available for converting the amorphous structure to a crystalline structure. Proof-of-concept p-n junction devices were fabricated in these chemically annealed materials, and they showed classical nanocrystalline Si solar cell type behavior.

INTRODUCTION

Chemical annealing technique, where one subjects very thin films of a-Si:H (2-3 nm) to various plasma treatments, and then grows a thicker film by doing multiple cycles of growth and annealing, has been used in the past to change the bandgap and H bonding of a-Si:H [1-4]. Chemical annealing of thin a-Si:H films has also been used to show that the amorphous films become more ordered when they are subjected to H plasma [5]. It has generally been assumed that one needs the reactive etching effect of H plasma in order to convert an amorphous film into a crystalline film, whether in layer-by-layer growth or by continuous deposition, where one achieves a similar effect by using high dilution ratios in hydrogen/silane mixtures. It is generally found that one needs a high dilution ratio (~20:1) to obtain good crystallinity in continuously grown Si films. However, recently we showed that at lower pressures, one can tolerate a lower hydrogen/silane ratio while still obtaining nanocrystalline films [6]. In this work, we carry the concept of controlled ion bombardment further, by using a non-reactive helium ion beam, to induce crystallinity in thin a-Si:H films, thus showing that it is not necessarily the reactive etching effect of hydrogen that is responsible for crystallinity.

DESCRIPTION OF EXPERIMENT

The film growth experiments were done in a low pressure, remote ECR reactor which has been described previously [7]. The films were grown at a temperature of 300 C, and pressures of 15-20 mTorr, from a silane-He-hydrogen mixture. The microwave power was 150 W. The flow rates were: silane =3 sccm, helium=36 sccm and hydrogen= 10 sccm. The hydrogen and silane were introduced near the substrate, whereas the helium was introduced in the remote plasma zone, about 30 cm away from the substrate. During the growth cycle, all three gases were flowing; during the annealing cycle, the silane and hydrogen were switched off and only helium was flowing. The plasma was kept on continuously. The time for growth was kept fixed at 10 s, whereas the anneal times were varied from 10 s to 60 s. The typical growth of the film per cycle was about 2 nm.

The films were characterized for their structure using a Renishaw Raman microscope, and x-ray diffraction. The grain size was obtained from x-ray diffraction using Scherer's formula.

STRUCTURE OF FILMS

In Fig. 1, we show the Raman data for a film which was subjected to 10 second anneal in a helium plasma (left figure), or a 30 second anneal (right figure). Quite clearly, the film subjected to a short anneal cycle is mostly amorphous, whereas the film subjected to longer anneal cycles shows classical crystalline peaks at 520 cm^{-1} . The ratio of the crystalline to amorphous peaks is $\sim 3.2:1$, implying a film that is about 70% crystalline.

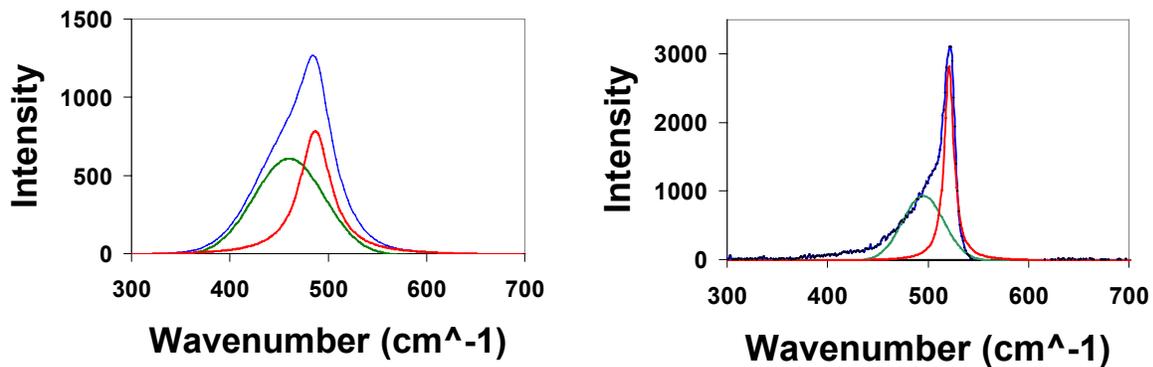


Fig. 1 Raman spectra of two films subjected to chemical anneal with He. The one on the left was subjected to 10s anneal, and one on the right, to 30 s anneal. The film on the right shows a significant crystalline fraction.

In Fig. 2 we show the ratio of crystalline to amorphous peaks as a function of anneal times. Clearly, the ratio increases with increasing anneal times and then saturates.

The corresponding x-ray diffraction spectra are shown in Fig. 3 for the case of 30 second anneals. In agreement with the Raman data presented in Fig. 1, the film subjected to 30 second anneal has a clear crystalline peaks showing the presence of both $\langle 111 \rangle$ and $\langle 220 \rangle$ peaks. In

common with most films produced using continuous ECR deposition, the $\langle 111 \rangle$ peak dominates. The grain size estimated from using Scherer's formula is 10 nm.

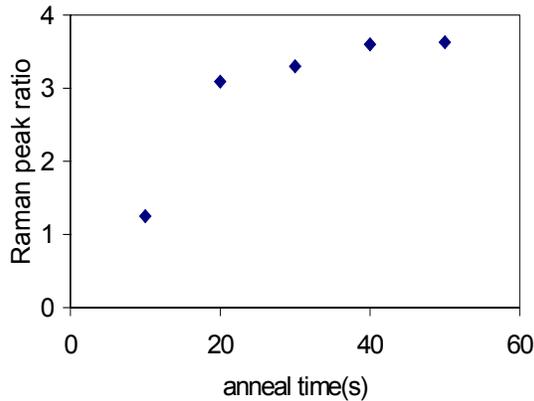


Fig. 2 Raman peak ratio as a function of anneal Time

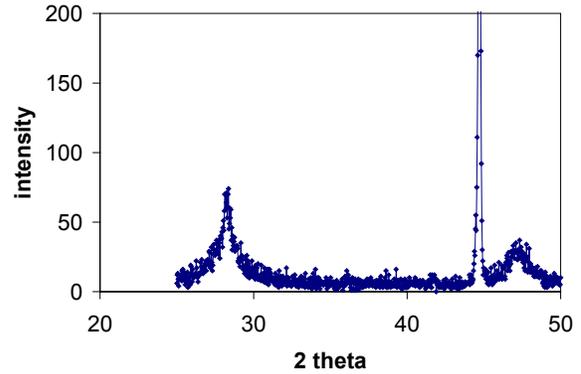


Fig. 3 x-ray data for film with 30 s anneal Both $\langle 111 \rangle$ and $\langle 220 \rangle$ peaks are visible The peak at 45° is due to steel substrate

In contrast to these results, when we used a hydrogen plasma beam instead of a helium beam during both deposition and annealing, the resulting films did not become nanocrystalline under comparable annealing cycles.

These results are remarkable, because they contradict the generally accepted assumption that high hydrogen dilutions are needed to crystallize the amorphous films. Instead, what we have shown is that it is the ion flux and energy in a beam that is responsible for crystallization, and that the residual hydrogen in an a-Si:H films is enough to cause any reactivity, such as removal of excess hydrogen from deep within the lattice. The reconstruction of bonds to a more ordered state seems to depend on the presence of ion flux and energy. Note that in the previous work of Miyazaki et al [5], an experiment with a He beam was not done; it is entirely possible that in their case also, it was the ion energy of a hydrogen plasma that was causing better ordering, rather than any reactivity. The present results support the recent results from our group which showed that at low pressures in a VHF plasma reactor (50 mTorr), one could obtain crystallization of amorphous films at much lower hydrogen dilution ratios (12:1) than normally used (20:1), but that at higher pressures (200 mTorr and 500 mTorr), one needed the higher hydrogen dilution ratios [6].

HDYROGEN BONDING DATA

We studied the hydrogen bonding in these materials by growing layers on polished Si wafers. In Fig. 4, we show the FTIR absorption data on two films, a layer-by-layer film subjected to a short (10s) anneal cycle (A), and a film subjected to 30 s annealing cycle (B). It is very clear from the data that the film subjected to a short cycle shows the classical FTIR signature of a prominent Si-H absorption peak at 2000 cm^{-1} , whereas the film subjected to a longer cycle shows the characteristic 2100 cm^{-1} peak generally found in nc-Si:H which is attributed to bonding at grain boundaries. Thus the H bonding data agree with the x-ray and Raman data.

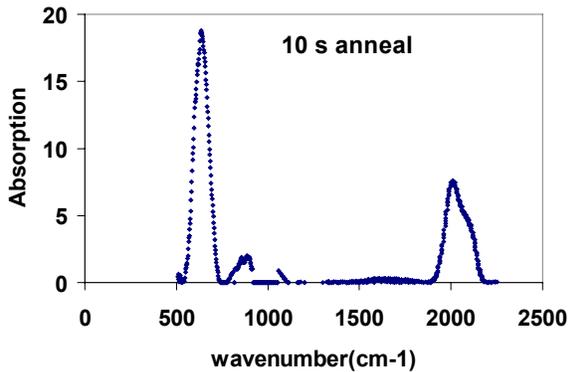


Fig. 4 (A) FTIR spectrum of CA film subjected to 10 s anneal cycle. The H peak at 2000 cm^{-1} is larger than at 2100 cm^{-1} , a signature of a-Si:H

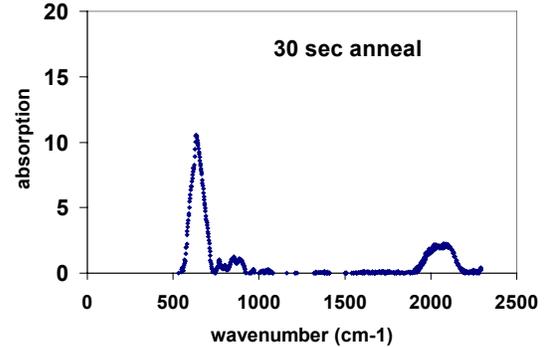


Fig. 4(B) FTIR spectrum of CA film subjected to 30 s anneal. The peaks at 2000 and 2100 cm^{-1} are approximately equal, 2100 being a signature of bonding at grain boundaries in nc-Si:H.

DEVICE FABRICATION AND RESULTS

In order to confirm that the nanocrystalline films produced using He annealing were of electronic quality, we fabricated simple solar cell devices. The devices were of the p+nn+ type, deposited on a stainless steel substrate [8]. The device structure is shown in Fig. 5. It consists of a back n+ a-Si:H layer, followed by a thin a-Si:H undoped layer. This thin layer seals up shorts, and also provides a back surface field to drive away holes from the rear n+ layer. The amorphous layer is followed by a nanocrystalline Si:H layer, grown using the chemical annealing recipe described above. The base n layer was followed by a top p+ layer made from nc-Si:H. A sputtered ITO contact completed the device.

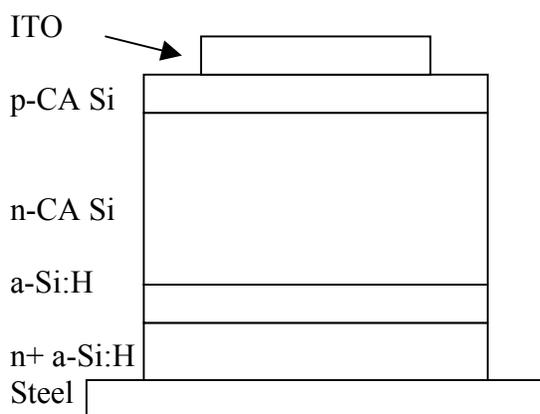


Fig. 5 Schematic diagram of solar cell

The results of the illuminated I-V curve are shown in Fig.6. They clearly show the characteristic voltage (0.5V) typical of nanocrystalline Si:H cells. The quantum efficiency data shown in Fig. 7 confirm that the cells are nanocrystalline, since the QE is going out to 800 nm.

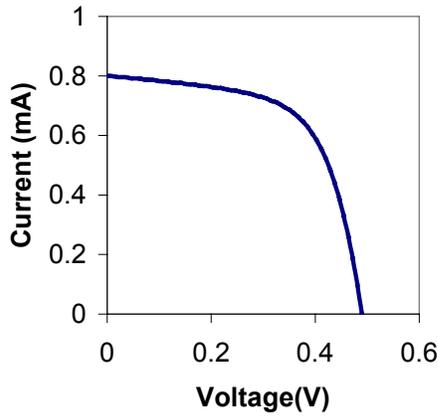


Fig. 6 Device I-V curve. Voltage of 0.5V indicative of nanocrystalline Si:H

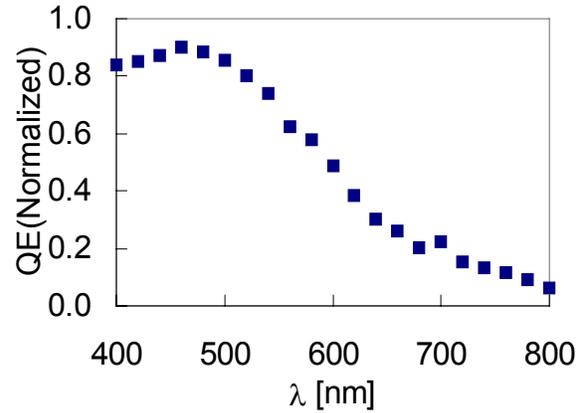


Fig. 7 Quantum efficiency of device. QE extending to 800 nm is indicative of nanocrystalline Si:H

CONCLUSIONS

In summary, we have shown that chemical annealing of a thin layer of a-Si:H by a helium plasma leads to crystallization of the film. This is remarkable result which shows the importance of ion bombardment on reordering of the structure of a-Si films. It contradicts virtually all the previous results which ascribe the crystallization phenomenon solely to the presence of excess hydrogen. Rather, these experimental results show that it may be a combination of ion bombardment and reactive etching which may be causing the crystallization of amorphous films when high hydrogen dilution is used.

ACKNOWLEDGEMENTS

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REFERENCES

1. H. Sato, K. Fukutani, T. Kamiya, C. M. Fortmann and I. Shimizu, Solar Energy Materials and Solar Cells, 66,321(2001)
2. W. Futako, T. Kamiya, C. M. Fortmann and I. Shimizu, J. Non-Cryst. Solids, 266,630(2000)
3. W. Futako, K. Yoshina, C. M. Fortmann and I. Shimizu, J.Appl. Phys. 85,812(1999)
4. K. Ohkawa,S. Shimizu, T. Komaru, W. Futako, T. Kamiya, C. M. Fortmann and I. Shimizu, Solar Energy Mater. And Solar Cells, 66,297(2001)
5. S. Miyazaki, N. Fukuhara and M. Hirose, J. Non-Cryst. Solids, 266,59(2000)
6. V. L. Dalal, J. Graves and J. Leib, Appl. Phys. Lett. 85, 1413(2004)
7. S. Kaushal, V. L. Dalal and J. Xu, J. Non-Cryst. Solids, 198,563(1996)
8. V. L. Dalal, Matt Welsh, Max Noack and J. H. Zhu, IEE Proc.-Circuits, Devices and Syst. 150, 316(2003)